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JC971 U.S. PTO 60/460096 04/03/03

# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

| INVENTOR(S) | | |
|---|---|---|
| Given Name (first and middle [if any]) | Family Name or Surname | Residence (City and either State or Foreign Country) |
| GERALD | SUGERMAN | ALLENDALE N.J. |

☒ Additional inventors are being named on the 1 separately numbered sheets attached hereto

**TITLE OF THE INVENTION (500 characters max)**

VOC FREE LATEX COALESCENT SYSTEMS

**Direct all correspondence to:** **CORRESPONDENCE ADDRESS**

☐ Customer Number ____ → Place Customer Number Bar Code Label here

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| | | | | | |
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**ENCLOSED APPLICATION PARTS (check all that apply)**

☒ Specification Number of Pages 6 ☐ CD(s), Number

☐ Drawing(s) Number of Sheets ☐ Other (specify)

☐ Application Data Sheet. See 37 CFR 1.76

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Respectfully submitted,

SIGNATURE Gerald Sugerman Date 4-3-03

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TELEPHONE 201 825 3479 Docket Number:

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## Additional Page

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Number 2 of 2

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# VOC Free Latex Coalescent Systems.

**Abstract:**
The usage of combinations of modest proportions of combinations of essentially nonvolatile, unsaturated ethers and / or esters, and small proportions of low glass transition temperature (Tg) latex reins, as replacements for volatile organic compounds (VOCs) as coalescents and optionally reactive amines (as replacements for conventionally employed volatile amines / ammonia neutralizers, respectively, has been found to enable the production of economical, low / no VOC-containing acrylic, styrenic copolymer, and vinyl copolymer latex based coatings, paints, and inks; which outperform their conventional counterparts. Further enhancement may be had via the substitution of zirconium based hyper-surfactants, in place of conventional soaps and / or detergents, in combination with the aforementioned nonvolatile, coalescent system, particularly in pigmented and / or reinforced coatings.

**Discussion:**
The usage of combinations of volatile amines as neutralizing agents / stabilizers, and of alcohols, glycols, ketones, and glycol monoethers and monoesters, at levels up to 40% of resin content, by weight, has been employed for more than fifty years to achieve the coalescence of latex solids in acrylic, styrenic copolymer polyvinyl acetate and related copolymer resins based coatings. The volatilization of these conventional neutralizers, and/ of coalescing components, after achieving film coalescence is normally required in order inhibit the resultant film's breakdown (reversion) in the presence of humid environments, and to provide acceptable wear and stain resistance to the dried film.

Recent concerns regarding the environmental degradation (predominantly low level ozone formation), and the health and fire hazards associated with exposure to volatile organics (VOCs), has led to increasingly strict regulatory limitations on the nature, and proportions of VOCs which may be employed in coatings.
One technique that has been employed in order to comply with said strictures in latex coating applications, is the development of self coalescing latex resins, employing significant proportions of olefinic monomers, (e.g. Airflex 809 Air products Corp.) which require minimal or no coalescents. Alternatively olefin-acrylate-vinyl co- and /or terpolymers have been blended with more conventional (incompletely compatable) acrylic and /or vinyl polymers and /or copolymers to produce bi/ multiphasic self coalescing polymer systems (e.g. Acronal S760 –BASF ) However, to date, such olefin monomer derived materials have been limited to low Tg film formers, with poor gloss, physical and chemical resistance performance properties. The instant disclosure provides technology which overcomes said deficiencies.
This invention relates to the use of low levels of combinations of, modest proportions unsaturated esters and /or ethers and low Tg latex resins optionally in combination with non-volatile reactive amines, as (partial or full) replacements for conventionally employed organic solvents as coalescents, and optionally volatile amines / ammonia neutralizers, respectively. Said usage not only effectively reduces emissions and enhances the performance of films produced from said conventional latex resins, but especially when employed in conjunction with certain types of hypersurfactants (cf. Table 3), also often

upgrades pigment / extender dispersion, and reduces grind times in particulate containing variants; thus enabling enhanced plant and energy use efficiencies.
A wide variety of low Tg resins may be usefully employed in the practice of this invention. Those most useful are materials having significant solubility (preferably complete solubility at the concentrations employed) in the resin or combination of resins employed as the major film former.

The non-volatile reactive amines useful in conjunction with the practice of this invention have vapor pressures below 1 mm Hg at 25 C, contain at least one each basic nitrogen, and at least one carbon to carbon double bond, and / or a transition metal ligand, and contain no more than twelve carbon atoms per basic nitrogen atom. Those more preferable, contain one or more (meth)acryl, N-allyl and /or N-vinyl ligands, and those most preferable have a water solubility exceeding 2% at 25 C. Specific examples of such useful non-volatile reactive amines are given in Table (A). Other embodiments of the invention include those specifically delineated in the tables and examples herein. These examples are intended to be illustrative rather than exhaustive of the scope of useful materials.

**TABLE A**

(AA) 4,4' bis N-vinyl pyrrolidone
(AB) N,N,N'- tris (2-butenyl), ethylene diamine
AC) N', methyl-1, 3-propylene diamine mono 2- propenamide
(AD) (N, 2- propenyl) bis (2-hydroxy) propyl amine
(AE) N, 2- propenyl, N'- (2-hydroxy) ethyl, hexamethylene triamine
(AF) 4-(N, 3-hydroxypropyl, N-vinyl) 2-amino ethyl 2-butenoate
(AF) 2-[N, (2-oxa -cyclopentadienyl)] amino acetic acid ethyl ester
(AG) 4-( N,N bis vinylamino) 1,3-pentanediol
(AH) tetraethylene glycol mono 3-( N, ethyl) amino, 2-(methyl) 2-propenoate
(AJ) N,N-divinyl glutamic acid 2- propenyl ester
(AK) 6-(N,N bis vinyl) hexanoic acid ethyl ester

The preferred types of unsaturated esters/ ethers / ether-esters useful in conjunction with the practice of this invention are those having vapor pressures below 0.1 mm Hg at 25 C, which are capable of, air initiated oxidative oligomerization / polymerization derived, non-reversible bonding, under normal latex application conditions, to film component(s) and /or to substrate, in order to maximize coating properties, via crosslinking the resulting latex thereby minimizing its (post film formation) environmental sensitivity. Examples of such unsaturated esters and ethers as are useful in the practice of the instant invention are provided in Table B. These examples are intended to be illustrative rather than exhaustive of the scope of useful materials.

**Table B**

(BA) trimethylol propane bis (2-methyl)-2-propenoate ester
(BB) sorbitan tetrakis 2-butenoate ester
(BC) bis penta erethyritol 2- propenolato, tris 2-propenoate ester
(BD) hexanoic acid 6-hydroxy, ( 2-propenoato)ethyl ester
(BE) citric acid tris isodecenyl ester
(BF) malic acid bis cinnamyl ester
(BG) 2,2- bis furoic acid 2-propenyl ester

(BH) 1,2,3-propane triol 1,3- bis vinyl ether, 2- phenyl carboxylate ester
(BJ) tris 2-butene diol mono (methyl) glutarate ester
(BK) ethoxylated (4) bis phenol A mono 2-propenoate ester

The surfactants most useful in conjunction with the practice of this invention are those having vapor pressures below 0.1 mm Hg at 25 C, which are capable of non-reversible bonding, under normal processing conditions, to film component(s) and /or substrate in order to maximize coating properties, while minimizing post film formation environmental sensitivity, which serve to efficiently wet substrates coated, and to disperse particulates, if any, employed in the formulated latex coating. Among the surfactants found to be useful in the practice of this invention, are amphoteric detergents, and certain organometalics based on tetravalent titanium or zirconium. These last have been found to contribute significantly to substrate adhesion and improved corrosion resistance on wood, metalic and ceramic substrates, and to be particularly useful in maximizing color intensities of carbon black, azo and phthalocyanine based pigments. Specific examples of the preferred types of hypersurfactants are given in Table C. These examples are intended to be illustrative rather than exhaustive of the scope of useful materials.

## Table C

(CA) zirconium 4 tetrakis oleylolato adduct one mole of bis (octyl) phosphite
(CB) zirconium 4 bis bis(2, 4- dioxo)undecanolato
(CC) zirconium 4 isooctanolato tris p-[3-N(methyl) morpholino]octyl phenyl phosphonic acid
(CD) zirconium 4 2-oxy propanoato, bis ( mono phenyl ether) triethylene glycolato
(CE) Titanium 4 octyl, [(tris octyl) diphosphato
(CF) zirconium 4 oxoethylene, bis (dodecyl) phenylsulfonato
(CG) oxy [bis zirconium 4 (bis tridecyl) diphosphate]
(CH) zirconium 4 tetraethylene glycol monomethyl ether, tris (tetraethylene glycol monomethyl ether) diphosphato
(CJ) 4- N-(methyl),N- octylamino, 1,4 –cyclohexadiene carboxylic acid
(CK) triethylene glycol diolato, bis [zirconium 4 tris (octyl) phosphato]

The low Tg cocalescents which are useful in the application of this invention are those with a Tg below 15°C, those most preferable have a Tg below 10°C. Tthe specific low Tg resin employed as a co-coalescenrt in any given formulation must be at least partially compatible with the latex resin(s) employed in film formation. In practice said restriction requires that the low Tg latex employed preferably be stabilized via the same charge type as the film former, except that Low Tg nonionic latexes may be employed in conjunction with anionic, cationic and or nonionic film forming latex resins. Examples of Low Tg resins useful in the practice of this invention are legion; however, for the sake of brevity, only 10 representative samples are provided in Table C. The substitution of functionally equivalent materials, e.g. of unsaturated analogous unsaturated amides, for a portion of the aforementioned unsaturated ethers, esters or ether-esters disclosed above, and / or halogenation of one or more of the species of components heretofore described as necessary to the successful practice of this invention is envisioned by this invention and such non-critical modifications, and/or combinations of relevant species types must be considered as within the scope of this disclosure.

**Table D**

(DA) Ethylene vinyl acetate[1]
(DB) Poly vinyl acetate[2]
(DC) Ethylene acrylate copolymer[3]
(DD) Poly isoprene[4]
(DE) Poly vinyl butyral[5]
(DF) Vinyl acrylic copolymer[6]
(DG) Polychloroprene[7]
(DH) Vinyl alcohol, acetatecopolymer[8]
(DJ) Ethoxylated bisphenol A[9]
(DK) Chlorinated, chlorosulfonated polyethylene[10]

Notes: 1) Airflex 809 (Air Products); 2) UCAR 371 (Dow) ; 3) Acronol 2367 (BASF); 4) IR401 Kraton Polymers; 5) Butvar Dispersion BR (UCB/Soluta); 6) Rhoplex 9100 (Rohm and Haas); 7) Neoprene WR (Dupont- Dow Elastomers); 8) Elvinil 51-05 (Dupont Dow); 9) Carbowax 2000 (Dow), 10) Hypalon 40 (Dupont-Dow Elastomers).

Further amplification of the scope and utility of the instant invention to latex coating applications in inks, paints and stains is illustrated by Examples 1 through 5. Said examples are intended to be illustrative rather than exhaustive of the extraordinarily diverse applicability of the instant invention. All references are expressly incorporated by reference in their entirety herein.

**Claims:**

What is claimed is:

1) A composition comprising a latex coating, an ink, or paint in which conventionally employed organic solvents used as coalescents are substantially or fully replaced by of a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters, and low Tg latex resins and in which, (optionally) nonvolatile reactive amines, may be employed to replace conventionally employed ammonia and or volatile amines, and/ or zirconium based organometalics may optionally be used as replacements for conventional surfactants.

2) A composition employed as a coalescent system for latex resins comprising a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters, and low Tg latex resins.

3) A compositions comprising nonvolatile reactive amines, and hydroxyl bearing, unsaturated esters/ ethers/ ether-esters in combination with low Tg latex resins, and hypersufactants derived from zirconium based organometallics, as replacements for volatile coalescents, and amines and conventional surfactants, respectively, in latex resin coatings, inks, and paints.

4) A composition employed as a coalescent system for acrylic latex resins comprising a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters, and low Tg latex resin(s), optionally containing from 0.2 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4% of essentially non-volatile reactive amine(s).

5) A composition employed as a coalescent system for vinyl, and or vinyl copolymer latex resins comprising a combination of from 1 to 15% essentially nonvolatile, unsaturated esters/ ethers/ ether-esters, and from 1 to 15% of low Tg latex resin(s), optionally containing from 0.1 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4% of essentially non-volatile reactive amine(s).

6) A composition employed as a coalescent system for styrenic coploymer latex resins a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters, and low Tg latex resin(s), optionally containing from 0.1 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4% of essentially non-volatile reactive amine(s).

7) A latex coating in which conventionally employed volatile amines / ammonia neutralizers, and organic solvents are substantially or fully replaced by of a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters. and low Tg latex resin(s), optionally containing from 0.1 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4% of essentially non-volatile reactive amine(s).

8) 8) A latex resin based ink in which conventionally employed volatile amines / ammonia neutralizers, and organic solvents used as coalescents are substantially or fully replaced by of a combination of essentially nonvolatile unsaturated esters/ ethers/ ether-esters. and low Tg

latex resin(s), optionally containing from 0.2 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4 weight % of essentially non-volatile reactive amine(s).

9) 9) A latex based paint in which conventionally employed volatile amines / ammonia neutralizers, and organic solvents used as coalescents are substantially or fully replaced by of a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters. and low Tg latex resin(s), optionally containing from 0.2 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4 weight % of essentially non-volatile reactive amine(s).

10) 10) A method for coalescing a latex resin comprising using a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters. and low Tg latex resin(s), optionally containing from 0.2 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4 weight % of essentially non-volatile reactive amine(s).

11) The method of claim 10, wherein the latex resin is a vinyl copolymer.

12) The method of claim 10, wherein the latex resin is a styrenic copolymer.

13) The method of claim 10, wherein the latex resin is an acrylic polymer or copolymer.

14) A method of making any one of a low VOC latex coating, paint, or ink, comprising using a combination of essentially nonvolatile, unsaturated esters/ ethers/ ether-esters. and low Tg latex resin(s), optionally containing from 0.2 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4 weight % of essentially non-volatile reactive amine(s).

15) A method of making any one of essentially VOC-void latex coating, paint, or ink, comprising using a combination of essentially nonvolatile
unsaturated esters/ ethers/ ether-esters. and low Tg latex resin(s), optionally containing from 0.1 to about 2 weight % of one or more zirconium based surfactants, and /or from 0.1 to about 4 weight % of essentially non-volatile reactive amine(s).